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Hydrogen Production from Hydrocarbon by Integration of Water–Carbon Reaction and Carbon Dioxide Removal (HyPr–RING Method)

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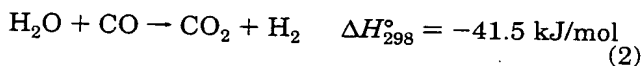
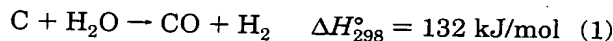
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A new hydrogen production method, HyPr–RING (Hydrogen Production by Reaction Integrated Novel Gasification), from organic compounds has been proposed. The fundamental concept of this process is integration of the water–hydrocarbon reaction, water–gas shift reaction, and the absorption of CO₂ and other pollutants in a single reactor. Hydrogen productivity from the reactions of organic material(s) with supercritical water was investigated in ranges of pressure 12–105 MPa and temperature 873–973 K by using a micro-autoclave. CO₂ was absorbed by a sorbent during the reactions in the micro-autoclave. It was found that H₂ and CH₄ as the major product gases can be produced from lignite, subbituminous, bituminous, and several organic wastes. For example, 170 cm³ of gas with about 80% H₂ and 20% CH₄ was produced from 0.1 g of the subbituminous Taiheiyo coal, at 923 K. In this case, about 90% of the carbon in the Taiheiyo coal was converted to produce H₂ and CH₄. Some organic materials including chlorine and sulfur, such as the poly(vinyl chloride) and the sludge, also produced gases that mainly contained H₂, CH₄, and no chlorine or sulfur gases.

Introduction

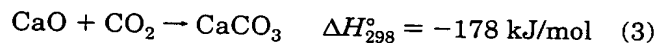
Hydrogen generates no pollutant, and supplies sufficient energy for power generation, transportation, and other applications. One of the hydrogen production processes is gasification of hydrocarbon such as fossil fuel and organic waste. Hydrocarbon is converted to hydrogen and carbon monoxide through the water–carbon reaction, as shown in eq 1. Carbon monoxide, CO, is then converted to hydrogen and carbon dioxide by the water–gas shift reaction, as shown in eq 2.



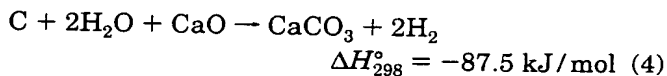
Reaction 1 is endothermic, about 1273 K or higher temperature is necessary to obtain a sufficiently fast reaction rate. In contrast, reaction 2 is exothermic and does not require such high temperatures to obtain a higher conversion of the CO, because it is governed by equilibrium ($K_C = P_{\text{CO}_2}P_{\text{H}_2}/P_{\text{H}_2\text{O}}P_{\text{CO}}$).¹ In most of the conventional processes,^{2,3} reaction 1 is performed in the

first reactor with an operating temperature above 1273 K. The produced gases are then introduced into the second reactor, which is usually operated below 673 K to perform the water–gas shift reaction (eq 2). However, the product of reaction 2 contains the CO₂, so that an extra separation process is required to obtain pure hydrogen.⁴

If the operating temperature of reaction 1 can be reduced and that of reaction 2 can be raised, reactions 1 and 2 can occur in the same reactor, and as a result the time and cost of the process can be reduced. To integrate the reactions in one reactor, we introduced CO₂ absorption reaction into the reaction system, as shown in eq 3:



The partial pressure ratio, $P_{\text{CO}_2}P_{\text{H}_2}/P_{\text{H}_2\text{O}}P_{\text{CO}}$, is decreased by the absorption of carbon dioxide. Thus, equilibrium of the reaction 2 may be kept at a higher temperature simultaneous with the CO₂ absorption. The expression of the overall reaction is written as follows:



This expression, eq 4, shows the new reaction system and also shows several possibilities: (1) H₂ is only a product of the gas phase; (2) relatively fast exothermic and catalytic reactions may occur at below 1173 K; (3)

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(1) Johnson, J. L. *Kinetics of coal gasification*; John Wiley & Sons: New York, 1979; p 261.

(2) Benson, H. E. *Processing of gasification products. Chemistry of coal utilization*, Second supplementary volume; John Wiley & Sons: New York, 1981.

(3) Longwell, J. P.; Rubin, E. S.; Wilson, J. *Coal: Energy for the future. Prog. Energy Combust. Sci.* 1995, 21, 269.

(4) Czuppon, T. A.; Knez, S. A.; Newsome, D. S. *Hydrogen. The Energy Technology and the environment*; Bisio, A., Boots, A., Eds.; John Wiley & Sons: New York, 1995; Vol. 3, p 1752.

Table 1. Properties of Coals and Organic Waste

coal	Proximate anal. wt %				ultimate anal. wt %, daf				
	vol.	moist.	FC	ash	C	H	N	O	Cl
Yallourn	47.3	14.3	37.6	0.8	66.1	5.3	0.6	27.7	
Taiheiyo	51.3	5.08	40.8	7.9	71.5	6.1	1.1	13.5	
Blair Athol (dry)	28.8		63.4	7.8	70.9	4.1	1.1	23.9	
BA 900 C char	1.23	1.89	86.3	12.5	97.4	0.68	0.68	0.94	
wood	79.5	8.62	11.7	0.2	51.0	6.4	0.11	42.5	
sludge	66.6	13.5	8.87	24.5	50.6	6.5	8.3	33.1	
poly(vinyl chloride)					37.8	6.3			55.9

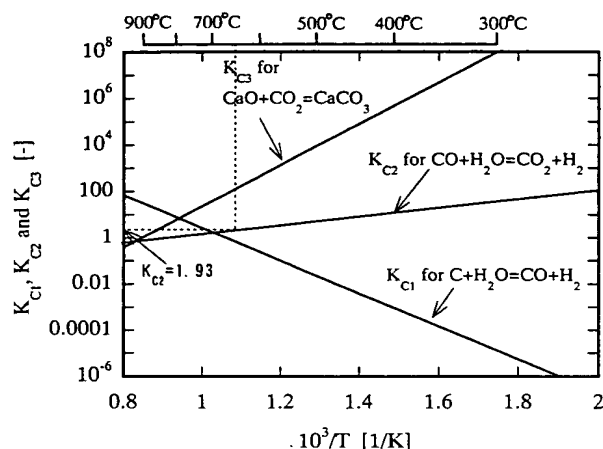


Figure 1. Equilibrium constants of reactions 1–3.

high H_2O partial pressure may enhance carbon conversion; and (4) CO_2 is fixed as a solid.

Accordingly, in this study, to confirm the advantages introduced here, optimum condition of the integration of reactions 1–3 and hydrogen productivity of several hydrocarbon materials, such as coals and organic wastes, were investigated theoretically and experimentally in the range of temperature 873–973 K and pressure 10–100 MPa.

Thermodynamic Discussion. Optimum temperature and pressure for the proposed reaction system is discussed on the basis of the thermodynamic data.⁵ Figure 1 shows the effect of temperature on the equilibrium constant, K_C , for reactions 1–3. The equilibrium constant of the endothermic reaction 1, K_{C1} , increases with the increase of the temperature. On the other hand, the equilibrium constants K_{C2} and K_{C3} decrease with the increase of the temperature because of exothermic reactions. K_{C3} is affected more strongly by the temperature than is K_{C2} .

The relations of the required pressure with temperature under equilibrium for reactions 1–3 can be evaluated in Figure 2 by re-plotting the data from Figure 1 and by assuming a desired composition in the product gases: 13.72% H_2 , 86.2% H_2O , 0.01% CO , and 0.01% CO_2 . The required pressure under equilibrium decreases with temperature for reaction 1, but increases with temperature for reactions 2 and 3. Reaction 3 dominates the whole of these reactions in the proposed reaction system in the temperature range from 673 to 1273 K. For example, 18.7 MPa is required at 973 K to obtain the assumed composition, as shown in Figure 2, while it increases up to 143 MPa at 1073 K. The

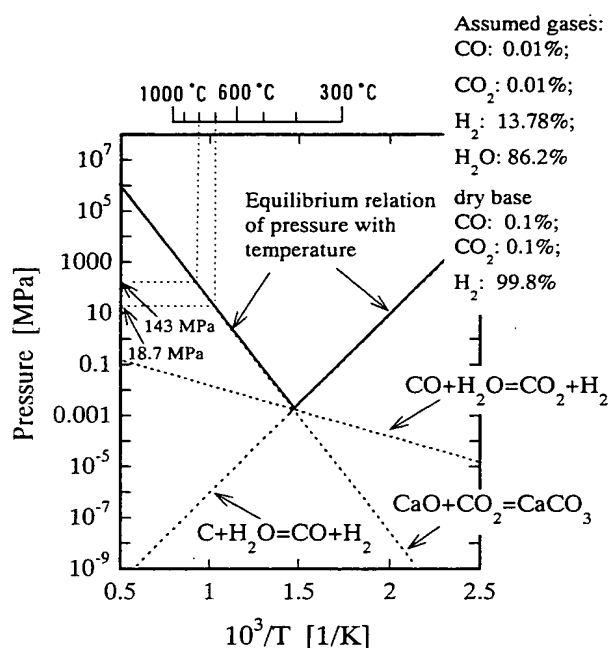


Figure 2. Relationship of the required pressure under equilibrium for the new reaction system.

required pressure strongly depends on the desired concentration of CO_2 in the product. For example, the required pressure for the reaction system drops to half of that in the case shown in Figure 2, when CO_2 concentration in the whole system is allowed to be double the amount shown.

Experimental Section

Taiheiyo coal (Japanese subbituminous), Blair Athol coal (Australian bituminous), and Yallourn coal (Australian lignite) were used in this study. several other organic wastes were also tested. Table 1 summarizes the results of proximate and ultimate analysis of these coals and organic wastes.

An autoclave used as a pressurized reactor is schematically shown in Figure 3 (inner volume, 20 cm^3). Temperature and pressure in the autoclave were measured by the K type thermocouple and a pressure transducer, respectively. Raw materials were crushed into about 0.1 mm for all experiments. $Ca(OH)_2$ powder was used for capturing the CO_2 as sorbent, and $NaOH$ was used as catalyst (Wako Pure Chemical Industries). First, 0.1 g of coal, 0.6 g of CO_2 sorbent, and 0.05 g of catalyst were mixed into the water, which was used to achieve the desired pressure at a certain temperature. Mixtures were fed into the autoclave, which was then inserted into the electric furnace and heated to the desired temperature with a heating rate of 20 K/min. After the desired temperature had been reached, it was maintained for a certain reaction period; in this case, for about 10 min.

After the reaction period had passed, the autoclave was removed from the furnace into room-temperature air and

(5) Barin, I. *Thermochemical data of pure substances*; VCH.: Verlagsgesellschaft mbH, D-6940 Weinheim (Federal Republic of Germany), 1989.

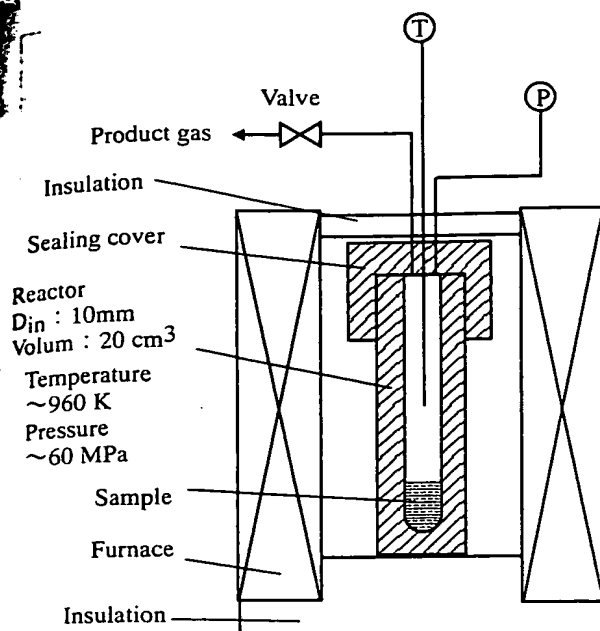


Figure 3. Micro-autoclave.

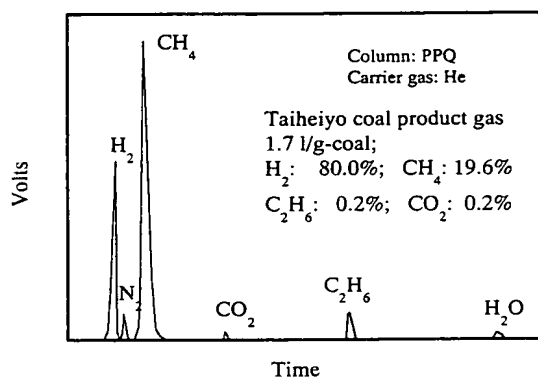
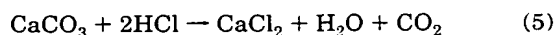


Figure 4. An example of TCD analysis for products gas from Taiheiyo coal experiment (923 K, 26 MPa).

cooled by a fan. When the temperature in the autoclave dropped to room temperature, the valve was opened to collect the product gas, and the sealing cover was removed to collect the remaining liquid and solid residues in the autoclave. After obtaining the product gas volume, the amount of the hydrogen and the other byproduct gases in the product gas would be quantified by gas chromatograph (MTI-Q30L).

Calcium carbonate, CaCO₃, in the residues was dissolved into HCl solution to release CO₂ in order to check the carbon balance:



The volume of CO₂ gas released from the sorbent was measured and the concentration of CO₂ gas was analyzed by gas chromatograph (MTI-Q30L). The unreacted carbon remaining in the residue was quantitatively determined by a CHN analyzer.

Results and Discussion

Figure 4 shows a gas chromatogram for the product gas from the Taiheiyo coal experiment at 923 K and 26 MPa. In this case, about 1.7 L/g-coal of product gas was

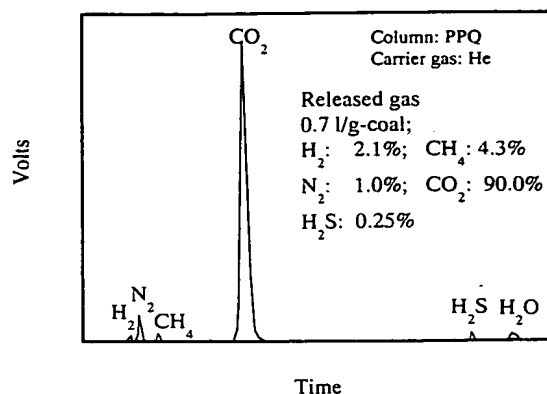


Figure 5. An example of TCD analysis for released gas from Taiheiyo coal experiment (923 K, 26 MPa).

produced. The product gas included 80% of hydrogen and 19.6% of methane. Trace amounts of CO₂ and C₂H₆ were detected, at concentrations of 0.2% each. Carbon monoxide and other hydrocarbon gases were not detected in the product gas. The concentration of CO in the product gas was calculated below 1.42 ppm by assuming that reaction 2 satisfied the condition for equilibrium. Figure 5 shows the gas chromatogram for the released gas from the residues. The total gas volume was about 0.7 L/g-coal, and 90% of the released gas was CO₂.

These results confirm the assumption of CO₂ capture by calcium oxide in the proposed reaction system. Further, the results prove the assumption that the CO is completely converted into hydrogen by adding CO₂ sorbent, yielding H₂ as a major product.

The ratio of oxygen to carbon, O/C, in the Taiheiyo coal is about 0.194, which means that possible CO₂ production by taking the oxygen in the coal is only 0.1 L/g-coal. This value is quite smaller than that of the CO₂ released from the residues. Most of the oxygen in the released CO₂ gas must be taken from H₂O, which is the only material containing active oxygen in the reaction system. The ratio of hydrogen to carbon, H/C, in Taiheiyo coal is about 0.0853. Possible hydrogen or methane production from atomic H in coal is about 0.7 L/g-coal H₂ or about 0.35 L/g-coal CH₄. These values are sufficiently smaller than those obtained in the experimental results. This means that most of the hydrogen and the oxygen in the product gases H₂ and CH₄, and released gas CO₂, must be obtained from H₂O. On the basis of the above, we can assume that reactions 1 and 2 certainly occurred in the same reactor. As shown in eq 4, the proposed reaction system produces two moles of hydrogen from one mole of the carbon. This relationship was confirmed by the volume of H₂, CH₄, and CO₂ in Figures 4 and 5.

Methane and ethane were found in the product gas for all experiments. The mechanism of the CH₄ and C₂H₆ formation has not yet been clarified. Perhaps they are formed by coal pyrolysis and H₂ reaction with carbon.

Carbon balance is calculated by measuring the carbon amount contained in the sample coal, the product gas, the released gas and the residue. Table 2 shows the three experimental results of the carbon balance for the Taiheiyo coals under the same conditions. The error was

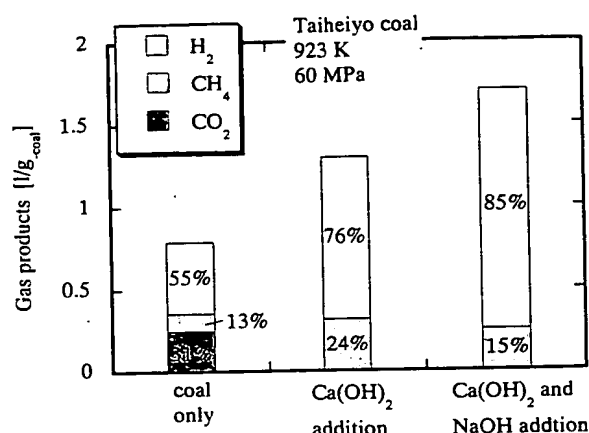


Figure 6. Effects of the CO₂ sorbent and the catalyst addition on gas products.

Table 2. Carbon Balance of Taiheiyu Coal Experiments (923 K, 60 MPa)

sample		before reaction $\times 10^{-3}$ [mol]	after reaction $\times 10^{-3}$ [mol]			error [%]	carbon conv. [%]
		C_{samp}	C_{prod}	C_{rel}	C_{res}	η_{er}	X
Taiheiyu	0.1 g	5.18	1.52	3.16	0.258	-4.67	90.3
Taiheiyu	0.1 g	5.18	1.27	3.34	0.513	1.10	89.0
Taiheiyu	0.1 g	5.18	1.38	3.45	0.395	0.87	93.3

calculated by eq 6:

$$\eta_{\text{er}} = \frac{(C_{\text{prod}} + C_{\text{rel}} + C_{\text{res}}) - C_{\text{samp}}}{C_{\text{samp}}} \times 100\% \quad (6)$$

where η_{er} is the error of carbon balance, C_{samp} , C_{prod} , C_{rel} , and C_{res} are the carbon content in the sample, the product gas, the released gas, and the residue, respectively. The error of the carbon balance for the Taiheiyu coal experiments is $\pm 5\%$. Conversion of the carbon of coal is also derived from the carbon contents, as follows:

$$X = \frac{C_{\text{prod}} + C_{\text{rel}}}{C_{\text{samp}}} \times 100\% \quad (7)$$

where X is the carbon conversion. The average carbon conversion of these experiments is calculated to be about 90%.

Figure 6 shows three experimental results to observe the effects of addition of the CO₂ sorbent, Ca(OH)₂, and the catalyst, NaOH, on gas production for the Taiheiyu coal: (a) no Ca(OH)₂ and NaOH were added into the system including the coal and the water; (b) only Ca(OH)₂ was added into the reaction system; and (c) both Ca(OH)₂ and NaOH were added into the reaction system. All experiments were performed at 923 K and 60 MPa. The amount of produced gas was only 0.8 L/g-coal for the first experiment, (a). The produced gas contained about 55% H₂, 13% CH₄, and 31% CO₂. About 0.2% CO was also observed in the product gas. The carbon conversion was only 31%. This result agreed with that of Heek and Muhlen⁶ in a study on coal-water or/

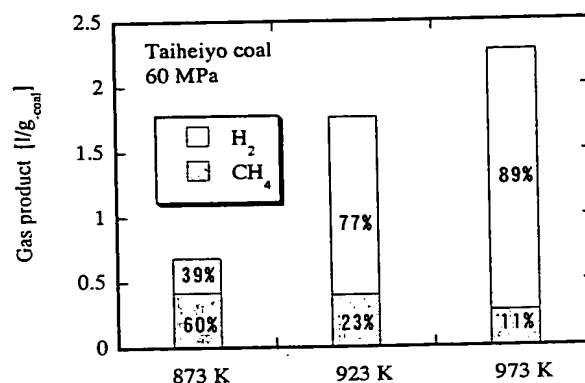


Figure 7. Effect of temperature on gas products.

and char-water reactions under high pressure. He reported that the reaction rate is very slow at temperatures below 1073 K and the rate does not increase significantly with pressure above 4 MPa.

For the second experiment, (b), the produced gas was increased up to 1.3 L/g-coal. Only 0.1% of the CO₂ was observed in the product, and CO was not detected by the gas chromatograph. Carbon conversion was 79.6% in this case and this value is much higher than that derived in the first experiment in which Ca(OH)₂ and catalyst were not used. The hydrogen production was also increased to 0.99 L/g-coal, which is almost twice that in the first experiment.

In the third experiment, (c), in which both the CO₂ sorbent, Ca(OH)₂, and the catalyst, NaOH, were added, the product gas was increased to about 1.70 L/g-coal, including 85% H₂, 15% CH₄, and only a trace amount of CO₂. The hydrogen production was increased to about 1.45 L/g-coal, which is three times that produced in the first experiment. The carbon conversion was about 90% in this case.

Ca and Na are well-known as good catalysts for the water-hydrocarbon reaction. Much research has been done to clarify the effect of catalysts on the coal or char-water reaction. The reported reaction rate is much higher than that without a catalyst.¹

Methane production was 0.104 L/g-coal for the first experiment, but it increased to 0.312 L/g-coal and 0.255 L/g-coal when Ca(OH)₂ and both Ca(OH)₂ and NaOH were added to the reaction system. Methane production was also enhanced by addition of the catalyst, Ca and Na.

The effect of temperature on the gas production is shown in Figure 7. Both Ca(OH)₂ and NaOH were added. At the comparatively lower temperature of 873 K, about 0.70 L/g-coal of gas was produced with a composition including approximately about 39% H₂ and 60% CH₄. The CO and the CO₂ were not detected in the product gas, which is considered due to the CO₂ absorption. In this case, the conversion of carbon in the coal was about 63.2%. When the temperature was increased to 923 K, 1.70 L/g-coal of gas was produced. In this case, the hydrogen content in the product was increased to 77% and the carbon conversion was about 90%. When the temperature was increased to 973 K, product gas increased to 2.1 L/g-coal and the hydrogen content increased to about 89%. Almost all of the carbon contained in the coal was converted into the product in this case.

(6) Heek, K. H.; Muhlen, H. J. Chemical kinetics of carbon and char gasification. *Fundamental issues in control of carbon gasification reactivity*; Lahaye, J., Ehrburger, P., Eds.; Kluwer Academic Publishers: Norwell, MA, 1991; p 1.

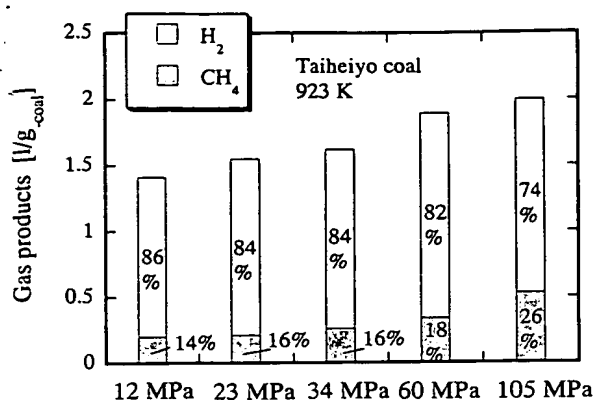


Figure 8. Effect of pressure on gas products.

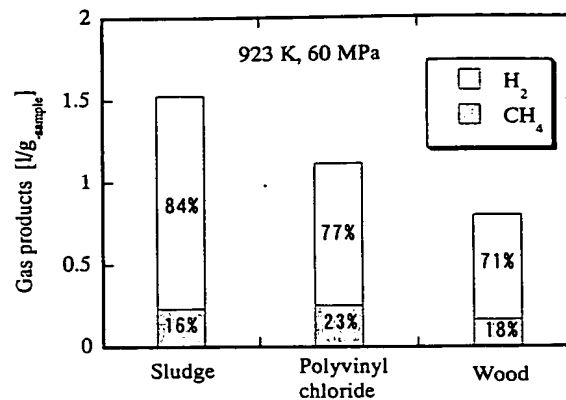


Figure 10. Gas products with various organic wastes.

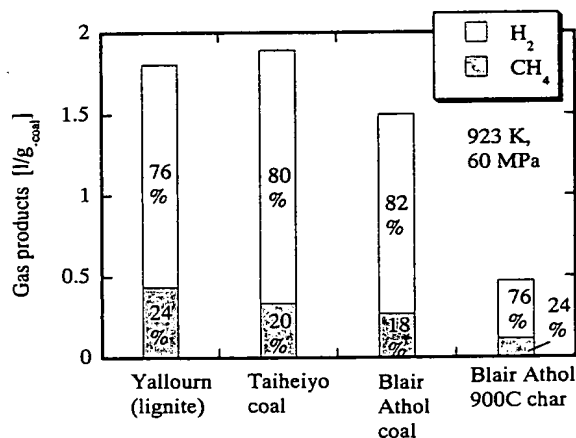
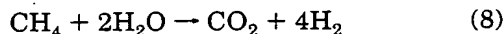


Figure 9. Effect of rank of coals on the gas products.

The composition of methane is decreased from 61% to 11% with the rise of the temperature, while that of hydrogen is increased from 39% to 89% with the temperature rise from 873 to 973 K. The CH₄ productions were 0.427 L/g-coal, 0.391 L/g-coal, and 0.265 L/g-coal for the temperatures 873 K, 923 K, and 973 K, respectively. Therefore, we consider that the methane production reaction is dominant at comparatively low temperatures and methane may be converted to hydrogen and carbon dioxide at higher temperatures by reacting with H₂O according to eq 8 as follows:

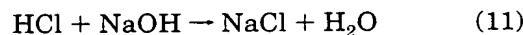
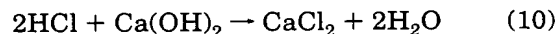
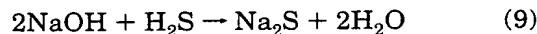


Pressure is also an important factor influencing gas production as shown in Figure 8. The total gas production and the concentration of CH₄ in the product gas increases with the increase in pressure. The H₂ production is decreased with the increase in pressure. However, the effect of pressure on hydrogen production is less influential than that of temperature.

Hydrogen production from various coals such as lignite, subbituminous, bituminous, and char are shown in Figure 9. As the coal rank order is raised from the lignite (Yallourn) to the subbituminous (Taiheiyo) coal, the production volume of the total gas and the hydrogen increases, because of the increase in the carbon content of the fuel. On the other hand, the opposite tendency is found in the case of the Taiheiyo coal and the Blair Athol

coal: that is, the total gas and the H₂ production reduces as the coal rank goes up. The reactivity of Blair Athol coal may be smaller than that of Taiheiyo coal.

Figure 10 shows the gas production for several organic wastes. Hydrogen is effectively generated from raw materials. It must be pointed out that the product gas did not contain H₂S and/or other forms of sulfur compounds, or chlorine, for any of these experiments, although these raw materials do contain some sulfur and chlorine. The sulfur and the chlorine may be captured (fixed) into salts by the NaOH or Ca(OH)₂ in the manner of the following reactions:



Conclusion

A new hydrogen production (HyPr-RING) method using organic compounds has been proposed. By combining the water-carbon reaction, the water-gas shift reaction, and carbon dioxide and other pollutants removal, all processes can be conducted in the single reactor under optimal conditions. The effect of various parameters on the hydrogen productivity was investigated for coals and organic wastes and the following results were obtained:

- (1) Addition of Ca and Na strongly affects hydrogen production and carbon dioxide capture.
- (2) Most of the hydrogen originates from the decomposition of the water, though some of it is generated from organic compounds.
- (3) Heteroatoms such as sulfur and chlorine contained in the organic materials are not detected in the product gas; they are captured by additives, such as Ca and Na.
- (4) Higher temperature and pressure increase the production of hydrogen, though temperature has a larger effect than pressure on hydrogen production.

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